



## Electrochemical properties of carbon-composite NASICON-type iron sulfate $\text{Fe}_2(\text{SO}_4)_3$ as a cathode for lithium secondary batteries

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### HIGHLIGHTS

- Mixing  $\text{Fe}_2(\text{SO}_4)_3$  with carbon improved its conductivity, capacity and cyclability.
- We studied to mixing methods of a conventional (CCT) and polymer added (PMCT).
- The capacity of non-treated sample of  $55 \text{ mA h g}^{-1}$  was improved by CCT to  $117 \text{ mA h g}^{-1}$ .
- In PMCT, carbonized polymer built a better mixture and doubles its cyclability.
- Particle size and distribution are keys to improve its capacity and cyclability.

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### ABSTRACT

We studied the effect of carbon treatment on improving the electrochemical properties (capacity and cyclability) of NASICON-type iron sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) for the cathodes of lithium ion batteries (LIBs). An optimized ball milling technique that was applied to a mixture of as-synthesized iron sulfate and conductive carbon ketjen black EC-600JD (KB) resulted a high capacity of  $117 \text{ mA h g}^{-1}$ , which is close to its theoretical capacity of  $134 \text{ mA h g}^{-1}$ . Moreover, the cyclability of coin-type test cell was doubled to 58 cycles by adding a polymer followed by heat treatment to the mixture of conductive carbon and  $\text{Fe}_2(\text{SO}_4)_3$ . The smaller particle size and more uniform distribution in the mixture of conductive carbon and  $\text{Fe}_2(\text{SO}_4)_3$  particles accounted for the improved electrochemical properties after treatment, as confirmed by FE-SEM observations.

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### 1. Introduction

Of the several electrochemically active compound materials containing transition metals that have been considered for use as the next generation cathodes for lithium ion batteries (LIBs), interest in iron-based compounds has increased because of their abundance and low cost. Many researchers have been attempting to find a high-performance iron-based electrode material by studying, for example,  $\text{FeOCl}$ ,  $\text{FeOOH}$ ,  $\text{FePS}_3$ ,  $\text{FeS}$ , [1] and  $\text{FeF}_3$  [2]. However, their results have shown that these iron compounds have relatively poor cyclability and a low discharge voltage, making them unsuitable for cathode applications.

Interest in studying polyanion based electrodes began after Goodenough [3,4] and Delmas [4] introduced the concept of three-

dimensional lithium intercalation using a polyanion  $((\text{XO}_4)^{n-})$  compound as an alternative to the closely packed oxygen atoms. This kind of polyanion was found to possess strong covalently bonded oxygen atoms [4,5] that offered better stability in terms of both shifting the temperature of oxygen release and heat generation to higher one. Since then, iron-based polyanion compounds such as  $\text{PO}_4^{3-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  have attracted the interest of many researchers [6]. However, due to the low potential of  $\text{Fe}^{2+/3+}$  in these iron-based polyanion compounds, layer-structure cathodes such as  $\text{LiCoO}_2$  were dominantly used for commercial LIBs.

On the other hand, in recent years several environmental and energy issues have triggered a shift in the use of LIBs from small-sized batteries for mobile applications to large-capacity batteries for both cycle usage (electric vehicles and smart grids) and back-up power usage. Although several safety measures have been employed with large cells, such as controlling the cut-off voltage using a battery management system and equipping the cell with

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a shutdown separator and valve tools, several issues still remain. In particular, safety concerns have been raised in relation to back-up applications, where the battery is kept in a stand-by condition, ready to meet a sudden demand. For this reason, a material that is stable at charge state (Li delithiation condition) is preferable. This is why iron phosphate ( $\text{LiFePO}_4$ ) with olivine is now applied as a cathode for large-capacity LIBs despite its lower energy density (capacity 150  $\text{mA h g}^{-1}$ , discharge voltage 3.5 V) [5] compared with other commercially available cathodes.

Another polyanion iron compound consisting of iron sulfate  $\text{Fe}_2(\text{SO}_4)_3$  with a NASICON structure has been suggested as a prospective material for the cathodes of LIBs because it has a flat profile at a high voltage of 3.6 V vs. Li metal and is easy to synthesize [6,7]. There are two kinds of NASICON-type iron sulfates that differ in terms of their monoclinic and hexagonal phase frameworks. Nanjundaswamy et al. [7] reported that although both phases provide a similar flat electrochemical profile, greater capacity fading was observed for the material with the monoclinic framework. Thus, our study was focused on the hexagonal type. A thermal study suggested that iron sulfate decomposes at temperatures above 600 °C, while a Co based layer type  $\text{LiCoO}_2$  cathode and a spinel type  $\text{LiMn}_2\text{O}_4$  cathode decomposes and releases oxygen at 250 °C, indicating that iron sulfate exhibits excellent stability at high temperature [1]. This is advantageous in terms of preventing the undesired heat release that might occur as a result of oxygen loss, even in an overcharged condition. However, there are still several technical problems, including low conductivity and the unavailability of lithium in the compound, with regard to using an iron sulfate cathode.

Carbon treatment has been used as an effective method for obtaining better electrochemical performance from active materials, namely, longer cyclability and a larger capacity. In particular, the existence of conductive carbon between the particles of an active material is favorable in terms of the electrochemical reaction because it enhances the electron transport [8]. Moreover, the conductive carbon that is present on the surface of an active material also protects the active material from direct contact with the electrolyte [8], thus avoiding any undesired surface degradation that might lead to poor cyclability. We studied a method of improving the electrochemical properties (capacity and cyclability) of NASICON-type iron sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) by applying two kinds of carbon treatment; the conventional carbon treatment (CCT) and the polymer modified carbon treatment (PMCT). The former was carried out with a dry ball mill to obtain a homogeneous mixture of active material and conductive carbon, while the latter was carried out with the addition of a polymer as a carbon source into a mixture of conductive carbon and active material, followed by heat treatment.

## 2. Experimental

### 2.1. Synthesis and characterization of NASICON type $\text{Fe}_2(\text{SO}_4)_3$

$\text{Fe}_2(\text{SO}_4)_3$  with a hexagonal framework was synthesized by thermal decomposition of ferrous ammonium sulfate hexahydrate

( $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Kanto Chemical Co., Inc.) in air at 500 °C for 10 h, as reported elsewhere [6,7]. The resulting powder was vacuum treated for at least 12 h before being stored in a dry room with a constant dew point of –50 °C. The structure of the obtained powder was characterized with an X-ray diffractometer (Rigaku, RINT2000), using  $\text{CuK}\alpha$  radiation under a constant power of 30 kV and 100 mA. The structural phases of the synthesized powder were identified using the database of the International Center for Diffraction Data (ICCD). Moreover, to estimate the ratio of carbon to active material, the elemental composition was analyzed using the following three methods; inductively coupled plasma combined with atomic emission spectroscopy (ICP/AES, Shimadzu Instrument, ICPS-8000) for Fe and S analysis, a flame spectrophotometer (Varian Spectra, SpectrAA-55) for Li analysis, and an infrared combustion analyzer (Horiba, EMIA-800) for C analysis. The particle morphology was observed using a field emission scanning electron microscopy (JEOL JSM-890). The sample was prepared by spreading the particle in the double-side carbon tape.

### 2.2. Carbon treatment

#### 2.2.1. Conventional carbon treatment (CCT)

Generally, during electrode preparation, active material is mixed with a conductive carbon such as acetylene black (AB), in order to assist the electron transfer between the particles. When we employed a conventional mixing method to mix the conductive carbon AB and active material iron sulfate by grinding, the capacity was only 55  $\text{mA h g}^{-1}$  (about 60% of its theoretical value). We assumed that this low capacity was because the active material iron sulfate and conductive carbon were insufficiently mixed. We studied two factors that were considered important in creating a uniform mixture of conductive carbon and active material iron sulfate, namely the type of conductive carbon and the mixing method.

First, we studied four types of conductive carbon; carbon nanotubes of C60 (CNT), maxsorb 3100 (Max), denka black (widely known in battery research as acetylene black (AB)), and ketjen black EC-600JD (KB), as given in Table 1. All the conductive carbons were pre-vacuumed for at least 12 h. The mixture of active material ( $\text{Fe}_2(\text{SO}_4)_3$  powder) to conductive carbon weight ratio was kept constant at 70:25. In the next step, we studied the effects of different mixing methods, namely grinding, mixing, and ball milling. The last evaluation involved in optimizing the ball mill conditions; i.e. rotation speed and mixing time.

After ball milling, the mixture of conductive carbon and the active material were sieved and stored in a dry room (dew point = –50 °C). This mixture was then subjected to a vacuum for at least 12 h before binder was added in preparing pellet electrode for electrochemical evaluation.

#### 2.2.2. Polymer modified carbon treatment (PMCT)

In this study, additional polymer was mixed together with conductive carbon KB and active material of iron sulfate through ball mill. The mixture was then heat treated to carbonize the polymer. The ball mill condition was the optimized one described in

**Table 1**  
Conducting carbon and the 5th discharge capacity for iron sulfate  $\text{Fe}_2(\text{SO}_4)_3$  with CCT.

Category	Product name	Abbr.	SSA ( $\text{m}^2 \text{g}^{-1}$ )	Average particle size ( $\mu\text{m}$ )	5th capacity ( $\text{mA h g}^{-1}$ )	Manufacturer
Carbon black	Ketjen black EC-600JD	KB	1270	0.03	117	Lion. Corp.
	Denka black	AB	68	0.03–0.04	104	Denki Kagaku Kogyou
Carbon nanotube	CNT-MTR	CNT	441	1.34	78	Material Technology Research (MTR), Ltd.
Alkaline activated carbon	Maxsorb 3100	Max.	3100	57	9	Kansai Coke and Chemicals

**Table 2**

The elemental weight percent and the correction factors for CCT, PMCT and the untreated sample.

Sample	CCT	PMCT	No treatment
Wt%			
Fe	20.3	21.1	27.7
S	17.3	18.3	23.3
C	25.1	22.1	—
O	34.9	36.3	47.6
Sum	97.6	97.8	98.6
Error	2.4	2.2	1.4
Correction factor	0.877	0.84	1 (no correction)

Section 2.2.1, in which the rotational speed was kept constant at a 200 rpm for 24 h. We used three kinds of polymer, polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG). The polymers used in this study are solids at room temperature, as can be seen from their glass transition temperatures ( $T_g$ ) given in Table 3 [10]. Since the particle sizes appeared to be important to obtain a homogeneous mixture, we ground and sieved the polymer before ball milling it with the conductive carbon and active material.

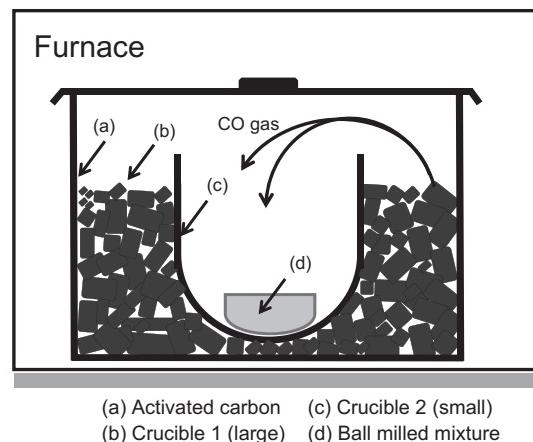
To find the optimum heat treatment condition we varied the temperature in the range of 150–450 °C and time in the range of 1–10 h. The heat treatment was carried out in a carbon-reduced atmosphere. The concept in using a carbon-reduced atmosphere is to create a reduced atmosphere through carbon combustion and to avoid sample oxidation during heat treatment. The experimental set up is shown in Fig. 1. We used two different sizes of aluminum crucible; a small one for the polymer added carbon and iron sulfate mixture, and a large one for the combusting carbon. The carbon we used for combustion was a granular form of activated charcoal (Kanto Chemical) with a particle size of 3.35–4.75 mm. This reduced atmosphere treatment is advantageous for a mass production because of its low cost.

Similar with the CCT samples, after ball milled and heat treated, the PMCT mixture was sieved and stored in a dry room (dew point = −50 °C). It was then subjected to a vacuum for at least 12 h before binder was added in preparing pellet electrode for electrochemical evaluation.

It is worth noting that since the carbonization process involves decomposing the polymer through heat treatment, the total weight ratio of active material to conductive carbon is changed by the treatment. An evaluation with a thermogravimetric analysis technique (TG/DTA, Rigaku, Thermoplus TG-8120) indicated that a weight loss of 20–30 wt% occurred during the heat treatment. This amount is larger than the amount of additional polymer that was kept constant at 15 wt%. Therefore, we assumed that the additional polymer was decomposed completely during the heat treatment, and moreover part of the conductive carbon was lost during the heat treatment process. The final ratio of active material to carbon was used to calculate the capacity of the sample after treatment.

### 2.3. Electrochemical characterization

The electrochemical characterizations were carried out using a coin-type test cell (type 2320). A polytetrafluoroethylene (PTFE)



**Fig. 1.** Schematic illustration of carbon-reduced heat treatment. The powder sample in the small crucible was set in the center of the crucible and surrounded with activated carbon.

binder was added to the mixture of conductive carbon and active material, with a mixture to binder weight ratio of 95:5, ground in an agate mortar and then roll-pressed into a 0.5 mm thick sheet to be installed in a coin-type test cell as a positive electrode. Lithium metal (0.3 mm thick) was used as a negative electrode. A microporous polypropylene film (Celgard) was inserted between the two electrodes as a separator. The electrolyte was 1 mol L<sup>−1</sup> of LiPF<sub>6</sub> in an equal volume of ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (Kishida Chemical, Co. Ltd.).

The entire preparation and test cell assembly process was carried out in a dry room (dew point = −50 °C). The electrochemical evaluations were performed in a constant temperature-controlled chamber ( $T = 20$  °C). The electrochemical evaluation was conducted at a constant current density of 1 mA cm<sup>−2</sup> in the 4.2 to 3 V range, with a rest period of 10 min between the charge and discharge steps. For each conditions carried out in the carbon treatments, we prepared 3 test cells to ensure the repeatability of our experiment.

The capacity of charge and discharge was estimated from the amount of active material existed in the measured pellet electrode, which contained active material (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), conductive carbon and PTFE binder. In a conventional electrode, where the active material and conductive carbon was ground, the ratio between active material and conductive carbon in the mixture was assumed to be constant before and after grinding. However, when the same assumption (a constant ratio of active material and conductive carbon) was applied to both CCT and PMCT, a capacity exceeding its theoretical value was obtained. Therefore, a correction factor, namely the ratio of iron (Fe) to carbon (C) before and after each treatment (CCT and PMCT), was applied to each of our measurements, as shown in Table 2. The weight percent of Fe, S and C data was obtained from the characterization of the elemental composition, while the O data were derived from a calculation by assuming the stoichiometry amount of the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The accuracy of each measurement was estimated to be 3%, which is within the measurement error range. The correction factor was determined

**Table 3**

Glass and melting temperatures for polymers used in the PMCT treatment.

Polymer	Abbr.	Mw (g mol <sup>−1</sup> )	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	5th capacity (mA h g <sup>−1</sup> )	Cycle number at 20% capacity fading
Polyvinyl alcohol	PVA	500	85	>220	130	58
Polyvinylpyrrolidone	PVP	40,000	120	180	127	43
Polyethylene glycol	PEG	6000	23–60	59	96	51
No addition (CCT sample)		—	—	—	117	38

from the weight ratio of  $\text{Fe}_2(\text{SO}_4)_3$  to conductive carbon before and after treatment. Elemental characterization was undertaken for as-synthesized  $\text{Fe}_2(\text{SO}_4)_3$ , CCT (200 rpm ball milling with KB for 24 h) and PMCT (ball milled with KB and PVA followed by carbon reduced heat treatment at 350 °C for 5 h).

### 3. Results and discussion

#### 3.1. Capacity improvement by CCT

Fig. 2 shows the as-synthesized NASICON type iron sulfate and a sample that was ball milled with KB conductive carbon. Both patterns correlated well with the standard pattern for  $\text{Fe}_2(\text{SO}_4)_3$  (PDF#33-0679), as shown in the bottom part of the figure. The Fe to S ratio for the pure and KB mixed samples evaluated using ICP/AES were 0.682 and 0.673, respectively. These values are close to the stoichiometry value of 0.667 with a measurement error of 2%. There was no significant change in either the structure or the chemical formula of the  $\text{Fe}_2(\text{SO}_4)_3$  before and after ball milled with KB conductive carbon.

Table 1 summarized the type of conductive carbon in influencing the capacity of iron sulfate. SSA is an abbreviation of specific surface area. The results indicated the small particle size and large SSA are key factors in selecting the conductive carbon. The carbon black (both AB and KB) appears to be favorable in improving the capacity. It is worth noting that KB tends to agglomerate due to its high porosity. For this reason, it is important to select a mixing-method that creates a well-dispersed KB. Among three kinds of mixing method that were studied, particularly ball milled exhibited a large capacity improvement (85 mA h g<sup>-1</sup> for a ball milled sample), as seen in Fig. 3. Our result, in which an improved capacity achieved by ball milling, is in a good agreement with the research trend in LIBs [8].

Janot et al. [9] mentioned that with ball milling, several factors such as the rotation speed and mixing time influence the resulting mixture. The effects of rotation speed (mixed for 24 h) and mixing time (at constant rotation speed of 200 rpm) are shown in Fig. 4(a) and (b), respectively. The discharge capacity for the 5th cycle for three different rotation speeds indicated that a fast rotation speed of 400 rpm resulted in poor cyclability, while 200 rpm provided a relatively stable cycle (Fig. 4(a)). Fig. 4(b) showed that a longer mixing time resulted in a significant capacity improvement, suppression of capacity fading, and better cyclability. After several

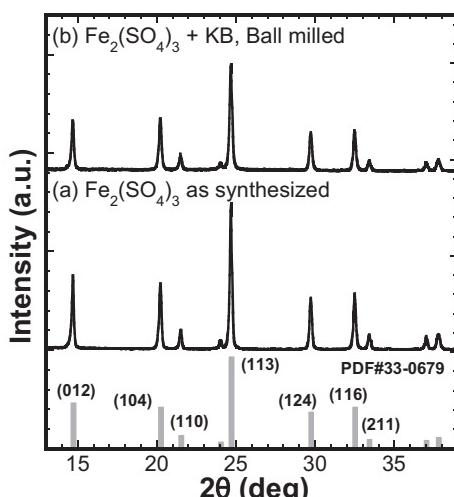


Fig. 2. XRD patterns for (a) as-synthesized  $\text{Fe}_2(\text{SO}_4)_3$  and (b) the CCT sample (mixture of  $\text{Fe}_2(\text{SO}_4)_3$  and KB conductive carbon that were 200 rpm ball milled for 24 h).

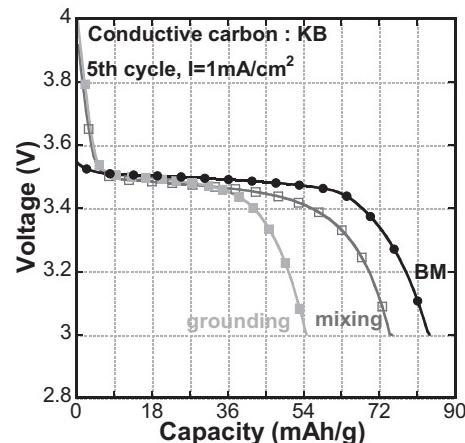


Fig. 3. 5th discharge curves for iron sulfate  $\text{Fe}_2(\text{SO}_4)_3$  that was obtained with different preparation methods; (a) grinding, (b) mixing, and (c) ball milling using KB conductive carbon. The current density was  $1 \text{ mA cm}^{-2}$ .

attempts, we found that the optimum condition was obtained by ball milling with conductive carbon KB under rotation speed of 200 rpm for 24 h. This optimized sample is denoted as a CCT sample.

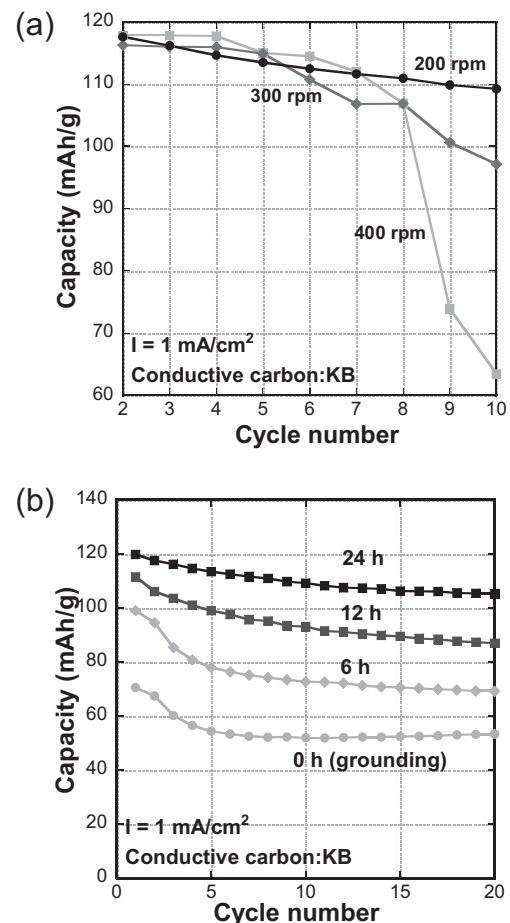
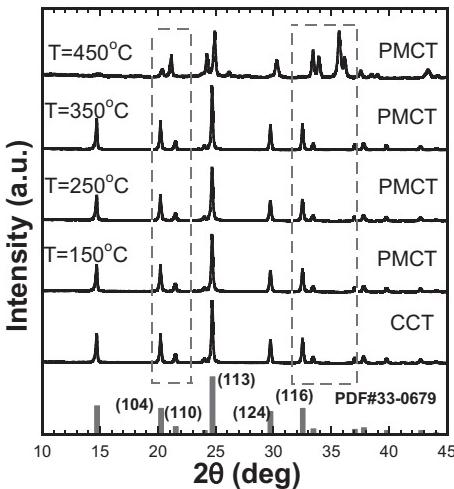


Fig. 4. (a) Cyclability dependence on ball mill rotation speed, treated for 24 h. The conductive carbon was KB and the current density was  $1 \text{ mA cm}^{-2}$ . (b) Cyclability dependence on ball milling times of 6, 12, and 24 h at a constant rotation speed of 200 rpm. The cyclability of sample prepared by grinding is shown for comparison.

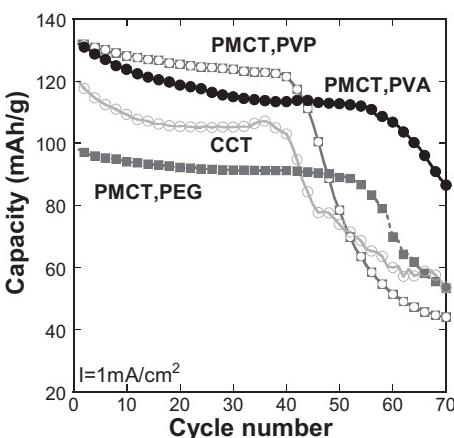


**Fig. 5.** XRD patterns of PMCT powder at various carbon-reduced thermal temperatures; 150, 250, 350 and 450 °C. The heat treatment was carried out for 5 h. The CCT sample (mixture of  $\text{Fe}_2(\text{SO}_4)_3$  and KB conductive carbon that were ball milled at 200 rpm for 24 h) is shown for comparison.

### 3.2. Cyclability improvement by PMCT

Fig. 5 shows the effect of heat treatment temperature on the crystal structure. The polymer used was PVA under a heat treatment in carbon reduced atmosphere for 5 h. For comparison, the XRD pattern of a CCT sample (after ball milling) is shown in the bottom part of the figure. For a mixture that was heat treated at 450 °C, in addition to having a lower intensity and broader peak, the main (113) peak was shifted and the secondary (012) peak disappeared. Since the  $\text{Fe}_2(\text{SO}_4)_3$  was synthesized at 500 °C, a heat treatment carried out in a temperature close to this might cause a decomposition of iron sulfate.

The effect of polymer-type on improving both the capacity and cyclability of  $\text{Fe}_2(\text{SO}_4)_3$  is summarized in Table 3. With the exception of PEG, which exhibited a capacity of  $96 \text{ mA h g}^{-1}$ , the capacities were improved with PVP and PVA to 130 and  $127 \text{ mA h g}^{-1}$ , respectively. Fig. 6 shows the dependence of cyclability on the polymer type. Although PVP and PVA revealed a similar improvement, it was clearly shown that PVA provided better cyclability. The cycle number for 20% capacity fading was originally



**Fig. 6.** Cyclability of iron sulfate after PMCT with various polymers; PVP, PVA, and PEG, compared with that for CCT (mixture of  $\text{Fe}_2(\text{SO}_4)_3$  and KB conductive carbon that were ball milled at 200 rpm for 24 h).

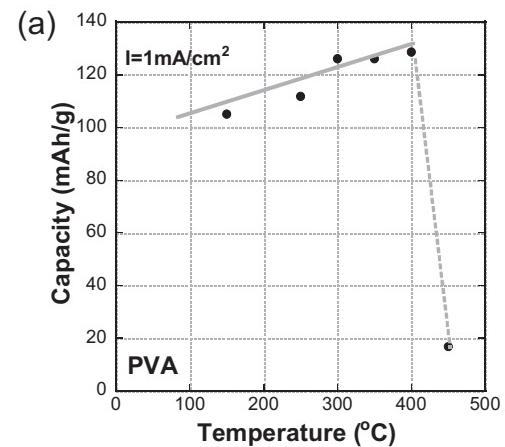
38 cycles for a CCT sample (optimized ball milled sample), and this was significantly improved to 43, 51 and 58 cycles by the addition of PVP, PEG and PVA, respectively.

In PMCT, heat treatment is important, since during this process, the polymer is decomposed and carbonization occurs. The effect of varying temperature (at a constant heat treatment time of 5 h) and time (at a constant temperature of 350 °C) for PVA is summarized in Fig. 7(a) and (b), respectively. A sudden capacity reduction that occurred for the sample treated at 450 °C was considered due to the decomposition of iron sulfate, as shown in Fig. 5. Moreover, Fig. 7(b) revealed that the capacity improved with a longer heat treatment of 1–5 h, but there was no significant improvement when the treatment lasted longer than 5 h. It appears that a treatment under temperature close to its  $T_m$  results in a better carbonization process, which ultimately leads to better electrochemical properties. This explained why the electrochemical properties were improved better when PVA was used.

The sample with PVA addition that was ball milled at a constant rotation speed of 200 rpm for 24 h followed by applying an optimized carbon heat treatment process of 350 °C for 5 h is denoted as a PMCT sample.

### 3.3. Particle morphology after treatment

The as-synthesized  $\text{Fe}_2(\text{SO}_4)_3$  was consisted of primary particles that agglomerated forming a secondary particle with an average size ranging between 5 and 10  $\mu\text{m}$ . Similarly, the as-received condition of conductive carbon KB tends to agglomerate as mentioned



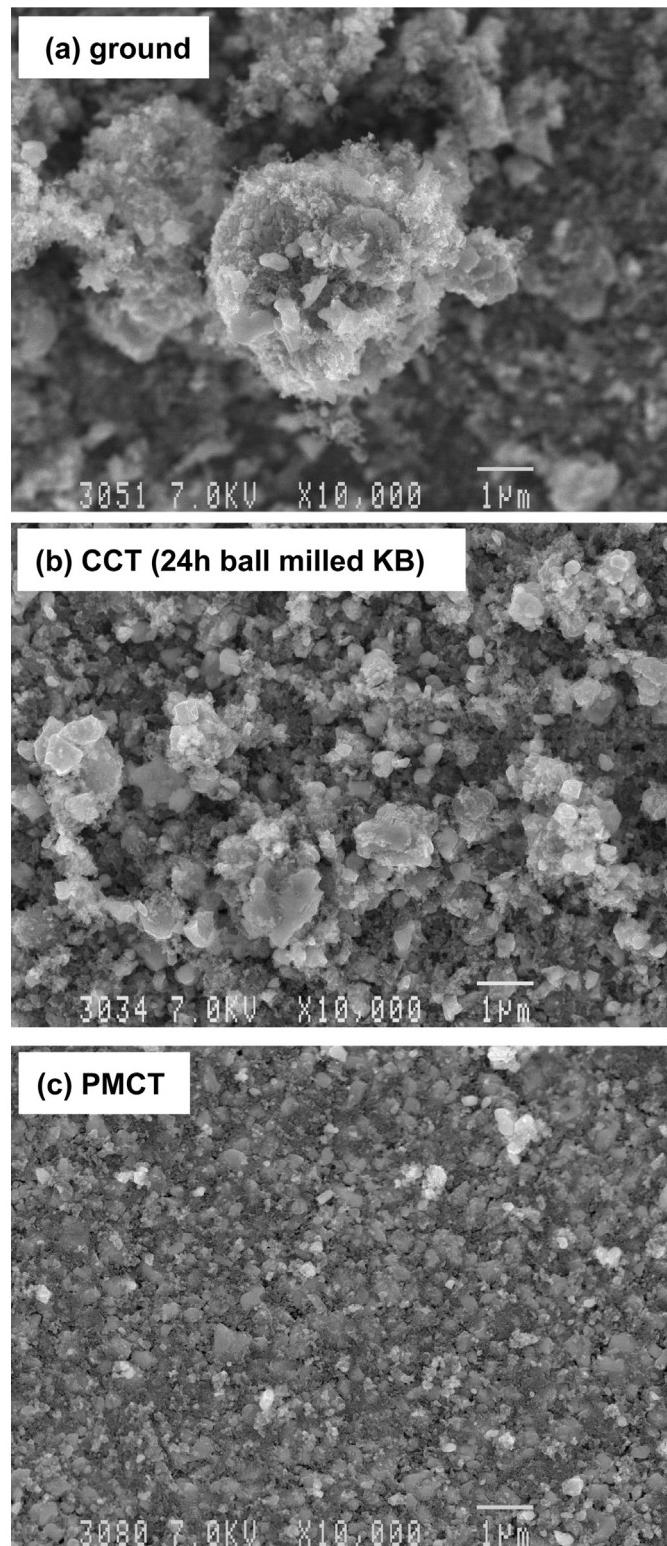
**Fig. 7.** Optimization of heat treatment conditions for iron sulfate after PVA based PMCT, (a) effect of temperature at a constant treatment time of 5 h, and (b) effect of treatment time at a constant temperature of 350 °C.

before. These agglomerated-forms in both  $\text{Fe}_2(\text{SO}_4)_3$  and KB were still existed after grinding (untreated sample), as can be seen in Fig. 8(a). The  $\text{Fe}_2(\text{SO}_4)_3$  appears bright (white), while the carbon appears dark (grayish). The conductive carbon in the mixture

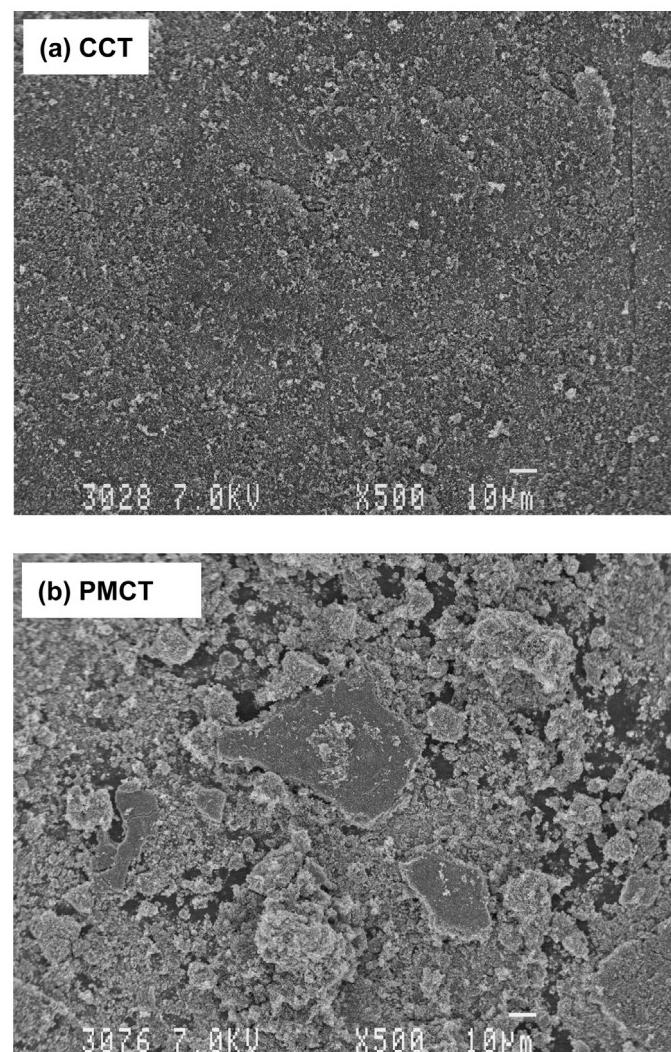
mostly existed on the surface of  $\text{Fe}_2(\text{SO}_4)_3$  particle, creating an undesired carbon-free region. The conductivity of this region is low and it is considered to be an electrochemically inert area, resulted an inferior capacity.

The homogeneity of mixture was improved with CCT and moreover with PMCT as can be seen in Fig. 8(b) and (c), respectively. Specifically, the conductive carbon KB was not only existed in the surface, as observed in the conventional grinding, but dispersed thoroughly in the mixture. We estimated the particle size was reduced to less than 8  $\mu\text{m}$  for conventionally ground sample to less than 1  $\mu\text{m}$  and less than 0.5  $\mu\text{m}$  for CCT and PMCT ones, respectively. This smaller particle size and well distributed conductive carbon in both CCT and PMCT are favorable because they minimized the undesired carbon-free areas that still existed in the conventional grounding method. This result agrees well with the study of olivine-type iron phosphate [8], in which a small particle-size and carbon treatment are the two key factors in improving the electrochemical properties.

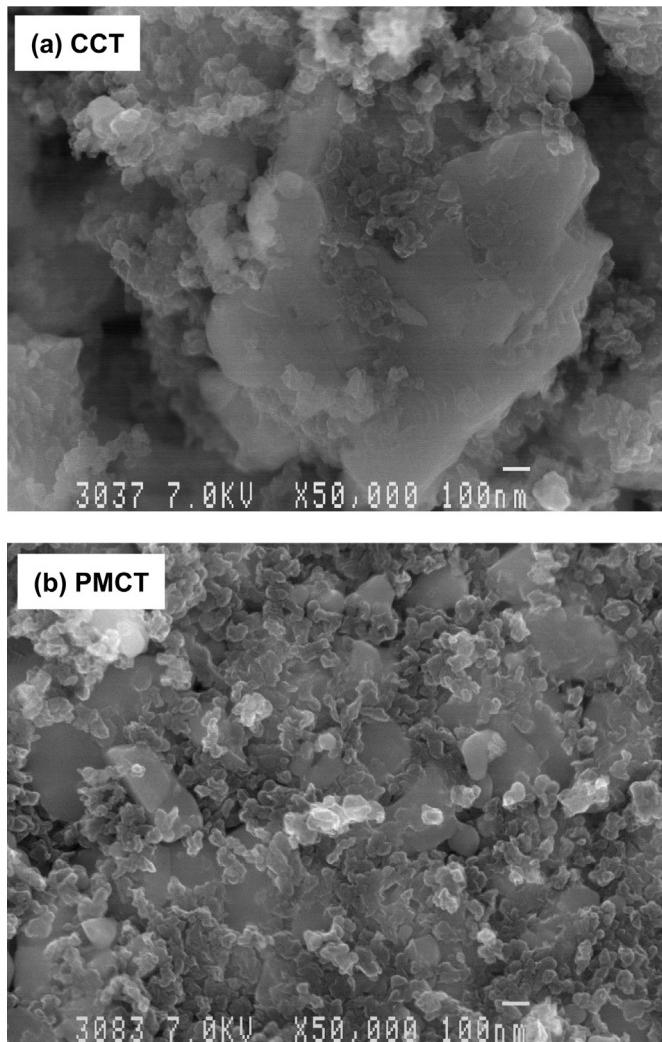
To clearly understand the differences between PMCT and CCT, we observed both their macroscopic and microscopic morphology shown in Figs. 9 and 10, respectively. The observations were carried out directly after treatment without sieving them. We observed several large agglomerations in the macroscopic view of mixture in PMCT (Fig. 9(b)), in contrast to the well-dispersed one in CCT



**Fig. 8.** Particle morphology observed with FE-SEM of (a) grinding, (b) CCT sample (mixture of  $\text{Fe}_2(\text{SO}_4)_3$  and KB conductive carbon that were ball milled at 200 rpm for 24 h), and (c) PMCT sample (mixture of  $\text{Fe}_2(\text{SO}_4)_3$ , KB conductive carbon and PVA, after ball milled and heat treated at 350 °C for 5 h).



**Fig. 9.** Low magnification particle morphology obtained by FE-SEM for a mixture of iron sulfate and KB conductive carbon after (a) CCT and (b) PMCT.



**Fig. 10.** Large magnification particle morphology obtained by FE-SEM for a mixture of iron sulfate and KB conductive carbon after (a) CCT and (b) PMCT.

(Fig. 9(a)). The polymer in PMCT, which dispersed in the mixture during ball milling, was softened and clustered during heat treatment at a temperature close to its  $T_g$  and  $T_m$ , respectively [10]. The clustered polymer was decomposed and carbonized during combustion process (above its  $T_m$ ) and finally it was solidified during cooling process to room temperature. These explained why large clusters were observed in PMCT (Fig. 9(b)). Moreover, it is worth noting that the clusters were fragile and very easy to be dispersed. In the electrochemical evaluation, these large agglomerations were not accounted because we sieved them before preparing pellet electrode.

A microscopic-scale observation was carried out to compare the surface condition among the conductive carbon and  $\text{Fe}_2(\text{SO}_4)_3$  active material. Fig. 10 indicates how well the conductive carbon KB was incorporated to the active material. In particular, the microscopic-view indicated that the homogeneity mixture among conductive carbon and  $\text{Fe}_2(\text{SO}_4)_3$  in PMCT sample (Fig. 10(b)) is superior than the one in CCT sample (Fig. 10(a)). From both the microscopic and macroscopic view of PMCT sample, we confirmed that the large cluster observed in the macroscopic scale consisted of a homogeneous mixture. Specifically, it can be seen that the surface of active material in PMCT was well-covered with carbon (both the

conductive carbon KB and additional carbon from polymer). In the early heat treatment process, the softened polymer might fill the remaining voids between conductive carbon and active material  $\text{Fe}_2(\text{SO}_4)_3$ . After heat treatment, this polymer carbonized and served as connector creating additional carbon network among the mixture, which is known as a composite. Apparently, the improved cyclability in PMCT was achieved because the contacts between particles of conductive carbon and  $\text{Fe}_2(\text{SO}_4)_3$  were improved.

This result indicates that the polymer has two roles. Besides serving as an additional carbon source [8], it also acts as a binder that serves as a template, which assists the formation of the composite between conductive carbon and active material. In other word, the PMCT provided two beneficial factors in improving electron transfer thus delivering a larger capacity as well as more stable cyclability. The first, is the formation of uniformly well distributed mixture that contained small particle size of  $\text{Fe}_2(\text{SO}_4)_3$  and conductive carbon. The latter is a formation of composite, in which the existence of carbon network serves to connect the conductive carbon and  $\text{Fe}_2(\text{SO}_4)_3$ .

#### 4. Conclusions

Two kinds of carbon treatment methods, CCT and PMCT, were applied to iron sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) powder. The conventional mixing method depends strongly on the particle size of the conductive carbon and the mixing condition. Several conditions: the mixing method, the carbon types, and the ball milling conditions such as time and rotation speed were studied. The optimized conventional method, denoted as CCT sample, was obtained by ball milling a mixture of  $\text{Fe}_2(\text{SO}_4)_3$  and conductive carbon KB for 24 h, resulted in a capacity of  $117 \text{ mA h g}^{-1}$  (5th cycle) and was stable up to 38 cycles. An optimized polymer modified sample, denoted as PMCT, was obtained when the  $\text{Fe}_2(\text{SO}_4)_3$ , KB and PVA were ball milled for 24 h followed by carbon-reduced heat treatment at  $350^\circ\text{C}$  for 5 h. The addition of polymer followed by carbonization during the heat treatment improved both capacity and cyclability. In particular, the added polymer was carbonized to form a composite with  $\text{Fe}_2(\text{SO}_4)_3$  and conductive carbon, which resulted in a capacity as large as  $130 \text{ mA h g}^{-1}$  that was stable up to 58 cycles.

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